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ON THE THEORY OF THERMAL DECOMPOSITION OF
DIATOMIC MOLECULES.

The process of thermal dissociation of diatomic molecules



was investigated by Rice^{1,2} and Careri^{3,4,5}. On grounds of the simple collision theory⁶ Careri suggested that dissociation of molecules occurs by direct transition from low vibrational levels in the bound state to the dissociation state. Theoretical calculations confirmed by direct experiment (see e.g. ref. 7) show, however, that energy transferred on molecular collisions with considerable probability is small, as compared to the dissociation energy D.

Calculating the dissociation rate of reaction (1) Rice^{1,2} reasonably postulated that the transition of molecules to the continuum energy state occurs from upper vibrational levels. However he did not take into account the perturbation of the Boltzmann vibrational distribution of molecule AB. This disturbance is one of the characteristics of thermal dissociation of diatomic molecules.

Perturbation of the Boltzmann vibrational distribution of dissociating molecules decreases the level population near the dissociation limit. This was shown to be connected⁸ with the rate of transition of greatly excited molecules to continuum states being very high as compared to molecular transition to the dissociation limit. Perturbation of the

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Boltzmann distribution is further increased as a result of decrease of vibrational quanta at the dissociation limit, the dissociation rate being determined by the rate of transfer of vibrationally excited molecules to upper vibrational levels.

Let $P_{k,k-1}$ be the probability per collision of transition from the vibrational level k to the level $k-1$. The probability of vibrational excitation of the molecule on transition $k-1 \rightarrow k$ can obviously be written as

$$P_{k-1,k} = P_{k,k-1} \cdot \exp(-E_{k,k-1}/kT)$$

where $E_{k,k-1}$ is the energy difference for levels k and $k-1$. If $x_k(t)$ is the distribution function, i.e. the population of k level, the kinetic equation will be x)

$$\frac{dx_k}{dt} = Z \left[\alpha_k P_{k,k-1} - (P_{k,k-1} + \alpha_{k+1} P_{k+1,k}) x_k + P_{k+1,k} x_{k+1} \right] \quad (2)$$

$$k = 0, 1, \dots, n$$

at boundary conditions $x_{-1} = x_{n+1} = 0$. Here Z is the collision number, i.e. the number of collisions per second suffered by molecules AB and M; $P_{n,n+1} \alpha_{n+1} = P_\infty$ is the probability of transition from the upper discrete level to the continuum energy state; $\alpha_k = \exp(-E_{k,k-1}/kT)$.

x) A system of equations similar to (2) has been studied by Montroll and Shuler⁹ in investigating the relaxation of a system of harmonic oscillators.

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Equations (2) are derived on assumption that only neighbouring transitions occur in the discrete energy spectrum and dissociation is possible only from the upper discrete level.

The general solution of eq.(2) is of the form¹⁰

$$X_k(t) = \sum_{m=0}^n c_k(\mu_m) \exp(-\mu_m t) \quad (3)$$

where $-\mu_m$ are eigenvalues of matrix B of the right side of the system of equations (2) (m enumerating these eigenvalues in increasing order of μ).

If $P_{\infty} = 0$ the eigenvalues of the corresponding matrix $B^{(0)}$ constitute the succession of $\mu_m^{(0)}$. Thermal equilibrium distribution corresponds then to the first eigenvalue $\mu_0^{(0)} = 0$.

If $P_{\infty} \neq 0$ then in accordance with the theory of local perturbations¹¹ all values of μ_m will be shifted in the same direction in relation to $\mu_m^{(0)}$. Thus $\mu_m > \mu_m^{(0)}$ when $P_{\infty} > 0$. If $\mu_0 \ll \mu_1$ then, as can be seen from (3), under condition $t \gg 1/\mu_1$ the distribution function decreases exponentially, which corresponds to decomposition. It follows from estimation that this inequality is fulfilled in most cases. In these conditions the lowest eigenvalue of matrix B can be found by expanding its determinant in the power series of μ and retaining only two terms.

Evaluation gives:

$$\mu_0 = Z / \left[\sum_{j=0}^n \exp(-E_j/kT) \sum_{s=k}^{n+1} \exp(E_s/kT) / P_{s,s-1} \right] \quad (4)$$

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The second sum in brackets of expression (4) does not considerably depend on the lower limit of summation because of the large increase of terms with S . The order of summation in eq.(4) can be changed and unity substituted for the lower limit of the sum over j . The sum over j becomes then equal to the vibrational partition function Q of the molecule AB. Taking into account that the equilibrium distribution function is defined by expression

$$x_k^{(0)} = \exp(-E_k/kT) / Q$$

eq.(4) can be rewritten to read

$$\mu_0 = Z / \left[1/x_n^{(0)} P_{n,\infty} + \sum 1/x_k^{(0)} P_{n,k-1} \right] \quad (5)$$

It can be shown that the value of the sum in eq.(5) is defined essentially by some of its maximum terms, their indexes $k, k-1$ corresponding to transitions between vibrational levels with energy difference $E_{k,k-1} \approx \frac{1}{2} h \omega_0 \sqrt{\frac{\kappa T}{2}}$ (ω_0 being the fundamental frequency of AB). Then expression (5) becomes:

$$\mu_0 = Z \frac{\frac{1}{2} h \omega_0}{\sqrt{2 \kappa T}} \cdot \exp(-D/kT) / Q \quad (6)$$

The decomposition rate constant k_d is equal to quantity μ_0 averaged over all rotational states of AB:

$$k_d = \int \mu_0(D_{\text{eff}}) \exp(-E_{\text{rot}}/kT) \frac{dE_{\text{rot}}}{kT} = G_{\text{rot}} \cdot \mu_0(D) \quad (7)$$

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where D_{eff} is the effective dissociation energy of the rotating molecule AB. As a result of the action of centrifugal forces D_{eff} becomes lower than D . Integration of (7) leads then to the appearance of an additional pre-exponential factor $G_{\text{rot}} > 1$.

Since the internal degrees of freedom of the molecule M were not taken into account, eq. (6) is valid only for the case of collisions between atomic molecules AB and atoms M. This can be exemplified by bromine dissociation:



Calculation of G_{rot} and integration by (7) gives $G_{\text{rot}} \approx 7$. Since owing to centrifugal extension of the molecule the number of collisions for a vibrationally excited molecule Z can exceed the gas kinetic collision number Z_0 by a factor of 2-4 and since the statistical weight of electronic states converging to the same dissociation limit D is 5,¹ estimation of the dissociation rate constant gives:

$$k_d = 5 \cdot 10^{-2} Z_0 \frac{D}{kT} \sqrt{\frac{2}{\pi}} \cdot \exp(-D/kT) / Q \quad (9)$$

Thus at $T = 2000^\circ\text{K}$ and taking the collision number as $Z_0 = 4.35 \cdot 10^{12} T^{1/2}$ c.c.m., we find in accordance with (9) :

$$k_d \approx 4 \cdot 10^{14} \exp(-D/kT) \quad (10)$$

The experimental value k_d for this temperature is ¹²

$$k_d = 5 \cdot 10^{14} e^{-D/kT} \quad (11)$$

Available data on rate constants at different temperatures (1000-1500°K) show that experimental values

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exceed theoretical ones not more than by a factor of 2-3.

Since dissociation is a complex multistage process involving consecutive stages of vibrational activation of molecules AB with their subsequent decomposition, the perturbation of Boltzmann distribution decreases the value of k_d as compared to that calculated from the equilibrium condition $(k_d)_{eq} = k_r K$, where K is the equilibrium constant of reaction (1). The recombination rate constant k_r should be approximately similar for non-equilibrium and equilibrium processes, since the rate of recombination is defined essentially by the rate of transition of two colliding atoms from the continuum energy state to one of the upper levels of the bound state. According to Willard ^{x)} the value of k_d for dissociation of Br_2 at $T = 300^\circ$ is

$$(k_d)_{eq} \approx 10^{16} \exp(-D/kT) \quad (12)$$

The value of k_d calculated by (9) for the same temperature is

$$k_d \approx 10^{15} \exp(-D/kT) \quad (13)$$

i.e. approximately by a factor of 10 lower than the equilibrium value. This distinction is connected therefore with the perturbation of equilibrium vibrational distribution of bromine molecules at the initial stage of reaction (8).

Some authors ^{1,14} have emphasized the high value of the

x) Cited from the paper of Palmer and Hornig¹².

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pre-exponential factor in the expression $(k_d)_{eq}$ for the dissociation rate of diatomic molecules, as compared to the collision number $Z_0 \approx 10^{14}$. This discrepancy is due to the persistence of equilibrium population of upper vibrational levels of AB (effect of the back reaction) and to the effect of molecular rotation. Moreover transitions from upper vibrational levels to the continuum energy state are likely to occur as a result of the action of long-range van-der-Waals forces. This can lead to a considerably higher value of Z , as compared to the gas kinetic collision number Z_0 . This conclusion is confirmed by evidence given in paper 13, establishing the dependence of k_{r_2} on the efficiency of van-der-Waals forces of molecules M of the third body. However the non-equilibrium process rate is not affected by long-range forces, since they govern the rate of dissociation from upper strongly excited vibrational levels, which is the fastest stage of the non-equilibrium process.

As can be seen from above, the value for the dissociation rate constant depends on product concentration, although k_d is usually defined as a true constant. It follows in turn that the conventional kinetic equation

$$-\frac{d[AB]}{dt} = k_d \cdot [AB][M] - k_r [A][B][M]$$

is not adequate for this process, since this equation does not render the distinction between k_d and $(k_d)_{eq}$.

It will be noted in this connection that the attempt

to describe by one interpolator expression both the values of k_d obtained by direct measurements of the non-equilibrium process (at high temperatures) and those calculated from the equilibrium condition (at low temperatures), as has been done for instance by Palmer and Hornig,¹² seems to have no physical sense.

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